



Full Length Article

Production of biodiesel from tannery waste using a stable and recyclable nano-catalyst: An optimization and kinetic study



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ABSTRACT

Biodiesel is produced from tannery waste by transesterification reaction in the presence of Cs₂O loaded onto a nano-magnetic core. The catalyst was prepared by co-precipitation followed by thermal oxidation method. The prepared catalyst was characterized using different analytical techniques. Further, the effectiveness of the prepared catalyst was determined by subjecting the fat from tannery waste to transesterification. Investigations were undertaken to determine the effect of the various process parameters influencing the process. Optimum conditions of 21:1 methanol-to-oil molar ratio, 7 wt% catalyst loading at 65 °C for 300 min with a constant stirring rate of 500 rpm produced a maximum yield of 97.1 wt%. The fuel properties of the biodiesel were analyzed as per ASTM test methods and compared with ASTM D6751 standard. Further, kinetic studies were conducted to know the rate of the reaction and its activation energy and frequency factors were identified as 43.8 kJ mol⁻¹ and 7.5 × 10⁴ min⁻¹ respectively.

1. Introduction

The depletion of hydrocarbon and the effects of global warming have forced researchers to look for alternative fuels [1,2]. The world energy demand continues to increase and the only possible way to surmount the challenge is by using biofuel. One such fuel that exhibits great potential is biodiesel. Biodiesel is, generally, a liquid renewable fuel derived from vegetable oils and animal fats. However, the direct use of these high viscous oils and fats in vehicle damages the engine, though the problem can be overcome by converting them into biodiesel (fatty acid alkyl ester) through esterification or transesterification reactions. This reaction is carried out using a catalyst and with the help of an alcohol [3]. The advantage of using biodiesel is its bio-degradability, non-toxic nature, lesser emission and environment friendliness [4,5].

The major drawback in the use of biodiesel is its economic factor. The price of biodiesel is higher than petro-diesel due to its high cost of raw material and operation. Feedstock selection plays a major role as it accounts for nearly 75–80% of the total cost [6,7]. Use of cost effective feedstocks such as waste cooking oil, non-edible oils, lard, algae, industrial waste lipid and waste fats will help in countering this problem

and a heterogeneous recyclable catalyst can reduce operating cost [8].

In tanneries, a large amount of solid wastes is produced during the pre-tanning of hides [9,10]. Treating these wastes is not cost effective and this poses economic burden to the tanneries. But these wastes have a high content of fat which can be extracted and used for biodiesel production [11–13]. The removal of fat not only reduces pollution caused by these wastes, but also generates revenue. The major challenge of using this as a feedstock for biodiesel is its large amount of contaminants. Moreover, the presence of these impurities prevents the use of conventional industrial catalysts which are cost effective and have a higher reaction rate. The contaminants cause soap formation with homogeneous alkali catalyst, causing difficulty in the separation of products due to the formation of emulsions [14]. Therefore, researchers are taking more efforts to find new heterogeneous catalysts that are not affected by impurities and also lessen the need for abundant water required for washing the product to remove homogeneous catalyst [15,16].

The identification of an appropriate heterogeneous catalyst aims to reduce the time needed for separating the catalyst from the product. The major drawback of a heterogeneous catalyst is its low rate of

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reaction due to the presence of three phases that induce resistance to mass transfer [17–20].

Thus, the focus is on using a reusable nano-catalyst that gives a higher yield, is easier to separate and also has a higher reaction rate [21]. They are produced by various methods such as co-precipitation, sol-gel, impregnation, chemical vapor deposition, electrochemical deposition and combustion. Among them, co-precipitation method generates nano-catalyst having high level porosity, active surface area and which consumes lesser time to produce nano-catalyst [22]. In line with these studies, Hu et al., (2011), synthesized KF/CaO-Fe₃O₄ recoverable magnetic nano-catalyst using sol-gel and incipient wetness impregnation method [23]. This catalyst successfully produced 95 wt% yield of biodiesel from stillingia oil. Similar study conducted by Guo et al., (2012) obtained a conversion of 99.6% by using a magnetic nano-catalyst (Fe₃O₄/Na₂SiO₃) which was then separated from the product mixture using a permanent magnet [24].

In the present investigation, fat extracted from tannery solid waste was used as a low cost feedstock. The physiochemical properties of the fat were analyzed as per standard methods. Further, a recoverable nano-catalyst (Fe₃O₄/Cs₂O) was synthesized by co-precipitation followed by thermal oxidation method. The prepared catalyst was characterized by SEM (Scanning Electron Microscopy), FTIR (Fourier Transform infra-red spectroscopy), XRD (X-ray diffraction spectroscopy) and particle size analysis. The catalyst was subjected to transesterification reaction to determine its catalytic activity. Subsequently, the various parameters affecting the biodiesel production process were optimized and their kinetic properties were determined. Finally, the produced biodiesel was characterized by ASTM methods and compared with ASTM D6751 standard.

2. Materials and methods

The tannery waste was collected from a tannery in Ranipet, Tamilnadu, India. The fat was extracted from the waste and the impurities present in it were removed by a modified preliminary treatment method as suggested by Balasubramanian et al. (2018) [25]. Then the dried fat was taken in a closed airtight container and used in further studies. The yield of the fat extracted from tannery waste was calculated using Eq. (1).

$$\text{Fat yield (wt\%)} = \frac{\text{Weight of fat extracted (g)}}{\text{Weight of tannery waste (g)}} \times 100 \quad (1)$$

Gas chromatography (GC) was used to identify the fatty acid profile of the fat from tannery waste. Hewlett Packard 5890 Series II GC instrument equipped with AlltechEcono-Cap SE-30 column and flame ionization detector was used to identify the fatty acids. The fat was initially converted into fatty acid methyl ester by Sodium methoxide-Methanol methylation process. The injector and detector port temperatures were maintained at 180 and 280 °C respectively. A carrier gas, helium, was used at a flow rate of 1 mL min⁻¹ with a split injection ratio of 1:50. The presence of fatty acid was qualified and quantified by comparing with the standard retention time and peak area of the individual fatty acid methyl ester. The average molecular weight of the fat was obtained from the fatty acid profile using Eq. (2). It was also used to determine the methanol to fat molar ratio during the transesterification process [26].

$$\text{Average molecular weight of fat} = 3 \sum (MW_i X_i) + 38 \quad (2)$$

where, MW_i and X_i represent the molecular weight and mole fraction of individual fatty acid respectively.

The physiochemical properties of the fat was determined by following the official methods of analysis of AOAC International [27]. The chemicals used in the study were of analytical grade and used as such without any further purification. All the chemicals were acquired from Sri Sashta Scientific Company, Coimbatore, India.

2.1. Preparation of magnetic nano-core

The conventional chemical co-precipitation method was followed for the preparation of magnetic nano-core (Fe₃O₄) in which, 250 mL of 12.5 g Fe₂SO₄·4H₂O and 24.1 g of FeCl₃·6H₂O were prepared separately using deionized water [23]. Then, the prepared solutions were mixed together in a beaker placed over a hot plate with a magnetic stirrer and heated above 60 °C. Subsequently, 1.33 g of cetyltrimethyl-ammonium bromide dissolved in 100 mL of distilled water was added to the mixture to carry out the reaction in colloidal suspension phase. The mixture was stirred continuously where 0.1 N NaOH was gradually added and the pH was constantly monitored. When the pH of the solution reached about 11.2, the addition of NaOH was stopped and the mixing was continued for 4 h at 60 °C. At the end of the reaction, the colour of the mixture changed from orange yellow to dark brown. The dark precipitate formed was separated and washed with distilled water with the aid of a permanent magnet.

2.2. Impregnation of Cs₂O with magnetic nano-core

Cesium chloride of a known concentration was prepared using 100 mL of ethanol and water (1:3 vol ratio). It was poured into a beaker containing 100 mL of Fe₃O₄ suspended in distilled water with cetyltrimethyl-ammonium bromide. The mixture was sonicated for 30 min, after which it was heated in a rotary vacuum evaporator for the solvents to evaporate. Finally, the dried mass of cesium chloride with magnetic nano-particles were scraped off and ground thoroughly. It was further calcinated in the presence of air in a muffle furnace at 600 °C and maintained for 1 h. An indigenously developed precise heating and cooling process were done at a rate of 1 °C min⁻¹ to reduce the demagnetization property. Under this thermal treatment, cesium chloride was converted to cesium oxide [28]. It was then cooled and the magnetized materials were separated using a permanent magnet and the prepared nano-catalyst (Fe₃O₄/Cs₂O) was used in further studies.

2.3. Characterization of Fe₃O₄/Cs₂O

Catalyst surface morphology was studied using SEM analysis for which a JSM 6360LA (JEOL, Japan) instrument was used.

The functional groups present on the surface of the catalyst were identified using an FTIR spectrometer. It was analyzed using a PerkinElmer Spectrum 100 FTIR instrument (PerkinElmer Inc., USA) having a universal diamond attenuated total reflectance sampling tool. For interpretation, infrared data were collected between the wavelength of 400 and 4000 cm⁻¹. Finally, the corrections in the obtained data were carried out by PerkinElmer Spectrum 10.4.2 analyzing software.

Phase identification of the catalyst was analyzed using X'pert Pro model, PAN analytical diffractometer instrument working on Cu Kα radiation source which was carried out in the scanning 2θ range from 10° to 80° having 0.02° as step size. Debye-Scherrer's relationship as shown in Eq. (3) was used to calculate the crystalline size of the sample.

$$T = \frac{0.94\lambda}{\beta \cos\theta} \quad (3)$$

where, T is the average particle size, λ is the X-ray wavelength, β is the full width at half maximum and θ is the diffraction angle.

Mastersizer 3000 laser scattering particle size analyzer (Malvern instrument Ltd., Worcestershire, UK) was used to determine the particle size distribution of the prepared catalyst. The size of the particles ranging from 10 nm to 3500 μm was measured.

The magnetic behavior of the synthesized catalyst was analyzed using a vibrating sample magnetometer (Cryogenic PT415, USA). A known quantity of Fe₃O₄ and Fe₃O₄/Cs₂O in dry powder form were loaded onto a separate sampling container and suspended in the magnetometer. Magnetization of the samples was measured between the

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